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SHOCK-TUBE MEASUREMENTS OF THE VIBRATION-VIBRATION ENERGY EXCHANGE PROBABILITY FOR THE CO-N$_2$ SYSTEM

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November 1970

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ABSTRACT

A shock-tube study was carried out to measure the vibration-vibration energy exchange probability, $P(\overset{10}{N_2}, \overset{}{\underset{01}{CO}})$, in N$_2$/CO/Ar mixtures. It was determined that at a temperature of about 4000°K, the measured probability, $P(\overset{10}{N_2}, \overset{}{\underset{01}{CO}}) \simeq 8 \times 10^{-3}$, agrees fairly well with the theoretical prediction of Schwartz, Slawsky, and Herzfeld (SSH), but that with decreasing temperature the measured probability falls considerably below the SSH theory prediction, i.e., $P(\overset{10}{N_2}, \overset{}{\underset{01}{CO}}) \simeq 4 \times 10^{-4}$ (measured) and $P(\overset{10}{N_2}, \overset{}{\underset{01}{CO}}) = 4 \times 10^{-3}$ (SSH), at 2000°K. The experimental results also demonstrate that over the temperature range 2000°-4000°K, argon and nitrogen are about equally efficient as translation-vibration collision partners for vibrational relaxation of CO, whereas, argon is between 2 and 3 times less efficient than N$_2$ for vibrational relaxation of N$_2$ molecules.

1. INTRODUCTION

In mixtures of diatomic gases relaxation of the vibrational energy modes of the molecules is primarily effected by two distinct types of collision processes: those that involve energy tranfer between the translational energy mode of one molecule and the vibrational mode of another, which are referred to as T-V processes, and those which involve direct energy exchange between the vibrational modes referred to as V-V processes. At low ambient temperatures, the rates of V-V processes have, for example, been measured using induced fluorescence techniques where the low translational energy of the molecules allows the influence of the T-V processes to be neglected. At higher temperatures the study of V-V processes is usually complicated by the contribution of the T-V processes to the overall relaxation rate. However, the contributions of the two processes can be separated under certain conditions, as was demonstrated in the shocktube experiments of Taylor, Camac, and Feinberg,[1] who used infrared emission techniques to measure V-V relaxation times in mixtures of NO-CO, NO-N_2, and CO_2-N_2.

In other shock-tube investigations of the vibrational relaxation of N_2,[2,3] CO has been used as an infrared active "seed", the assumption being that since the vibrational level spacings of N_2 and CO are close to resonant ($\Delta\omega_e \simeq 187$ cm^{-1}), the vibrational temperature of the CO would be closely coupled to that of the N_2. Thus, the infrared emission from the CO may be used to infer the vibrational temperature history of the nitrogen.

Unfortunately, very little or no experimental information has been available on the V-V exchange probabilities for the N_2-CO system above room temperature. Even at room temperature the reported values scatter by well over an order of magnitude. The few data points recently obtained in the shock-tube investigation by Sato, Tsuchiya, and Kuratani[4] over the temperature range 1750°-2300°K, were claimed to agree with the predictions of the Schwartz, Slawsky, and Herzfeld[5] (SSH) theory. However, our own calculations based on the SSH theory suggest that the values of the V-V exchange probabilities calculated by Sato, Tsuchiya, and Kuratani were too low by almost a factor of ten in the temperature range of their experiments.

In this paper we report the results of a shock-tube investigation from which we were able to determine V-V energy exchange probabilities for the N_2-CO system over the temperature range 2200°-4000°K. Our results show that close to 4000°K, the measured probabilities and the predictions of the SSH theory are in fair agreement, but that with decreasing temperature the probabilities fall considerably below the SSH theory prediction. Our results agree fairly well with those of Sato et al., and appear to extrapolate quite well through the bulk of the most recent data obtained over the temperature range from 1000°-2000°K by von Rosenberg, Bray, and Pratt.[6] In addition to the V-V energy exchange probabilities, our results also demonstrate that argon and nitrogen are about equally efficient as T-V collision partners for the vibrational relaxation of CO, whereas, argon is clearly less efficient than N_2 as a T-V collision partner for the vibrational relaxation of N_2 molecules.

2. EXPERIMENTAL METHOD AND APPARATUS

The experiments were carried out in a conventional pressure driven, 3 in bore, stainless steel shock-tube which has been described elsewhere.[7] The entire system could be evacuated to a pressure of 10^{-6} torr, with a typical degassing plus leak rate equivalent to a rate of pressure rise somewhat less than 10^{-4} torr per minute. Helium was used as the driver gas.

All of the test gas mixtures contained 2.5 mole percent of CO which ensured that the gas was optically thin to the fundamental emission band of CO over the temperature and pressure range of the experiments. The nitrogen concentration was varied between 37.5 and 5.0 mole percent with the remaining fraction being made up Matheson prepurified grade argon. The carbon monoxide and nitrogen used were research grade gases supplied by Lif-O-Gen.

The experimental observations were made behind reflected shock waves. This method of operation was adopted for two reasons. Firstly, since the gas behind the reflected shock close to the end wall is virtually stagnant, no "particle-time" boundary layer corrections need to be taken into account in the interpretation of the measurements, as is often the case in shock-tube investigations where observations are confined to the region follow-ing the primary shock. Secondly, in this particular type of investigation where the vibrational relaxation region is characterized by two decay times corresponding to an initial region of rapid relaxation followed by

a slower one, we found that it was possible to temporally resolve both regions behind the reflected shock wave, whereas, in the investigations to which we previously referred,[1,4,6] the initial relaxation region was not clearly resolved. In order to use the reflected shock wave region, two lithium fluoride windows, flush-mounted with the inside bore of the tube, were positioned at the end of the shock tube so that optical observations could be made along a tube diameter close to the end wall. A collimation system consisting of suitably placed optical stops allowed an indium antimonide photovoltaic detector to view radiation emanating from a well-defined volume of gas extending across the tube close to the plane of the end wall. The spatial resolution of the detector in both the axial and lateral planes of the shock tube was about 2 mm, and the axis of the collimation system was 5 mm in front of the end wall. An interference filter placed in front of the detector provided an effective pass band covering the spectral range from 4.0-5.5 μ.

In all of the experiments simultaneous records were obtained of the infrared emission profile and the reflected shock pressure at the end wall. The latter was measured using a Kistler type 603L pressure transducer together with a 70 db per octave Tchebbycheff filter to damp out the high frequency (∿ 300 KHz) microphony effects. It was noted that if the test gas contained more than 40 mole per cent of diatomic gases, the effects due to bifurcation of the reflected shock wave were clearly observed on both the infrared emission and pressure profiles within the time scale of the measurements. Bifurcation of the reflected shock wave
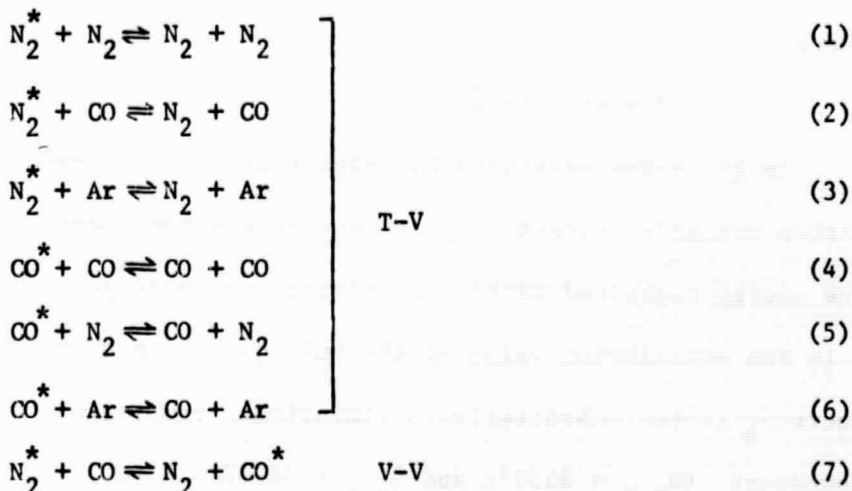
caused the initially constant pressure profile at the end wall to develope

a positive ramp, with an associated increase in the infrared emission

intensity.

As we reported in an earlier investigation,[8] care must be taken

in shock tube experiments involving CO to ensure that there is no impurity

radiation contributing to the fundamental emission in the 4-5.5 μ region.

Impurity radiation, which was thought to be due to water vapor scavenged

from the shock tube walls, was reduced to below detectable levels by

firing clean up shots into either pure argon or N_2-Ar mixtures. Subsequent

data shots were then recorded under the same test conditions using gas

mixtures containing carbon monoxide.

3. RELAXATION KINETICS

For our test gas mixtures consisting of CO, N_2, and Ar, it was assumed that the vibrational relaxation of the molecules could be described by the following set of energy transfer reactions:

$$N_2^* + N_2 \rightleftharpoons N_2 + N_2 \tag{1}$$

$$N_2^* + CO \rightleftharpoons N_2 + CO \tag{2}$$

$$N_2^* + Ar \rightleftharpoons N_2 + Ar \tag{3}$$

$$CO^* + CO \rightleftharpoons CO + CO \tag{4}$$

$$CO^* + N_2 \rightleftharpoons CO + N_2 \tag{5}$$

$$CO^* + Ar \rightleftharpoons CO + Ar \tag{6}$$

T-V

$$N_2^* + CO \rightleftharpoons N_2 + CO^* \qquad V\text{-}V \tag{7}$$

where the asterisk denotes a vibrationally excited molecule and any vibrational energy deficit, or surplus, in the V-V process (reaction (7)) is understood to be absorbed by the translational energy mode.

Schwartz, Slawsky, and Herzfeld[5] have derived the vibrational relaxation equations for a system consisting of two diatomic species. Their results may be simply modified to include the effects of the argon used in our experiments (reactions (3) and (6)), to give the following relaxation equations:

$$-\frac{dX_N}{dt} = \left\{ \frac{\psi_N}{\tau_1} + \frac{\psi_C}{\tau_2} + \frac{1 - \psi_N - \psi_C}{\tau_3} \right\} X_N$$

$$-\frac{\psi_C}{\tau_7} \left\{ \frac{X_C(1 - X_N)}{1 - \exp(-\theta_N)} - \frac{X_N(1 - X_C)}{1 - \exp(-\theta_C)} \right\} (1 - \exp(-\theta_N)) \tag{8}$$

and

$$-\frac{dX_C}{dt} = \left\{ \frac{\psi_C}{\tau_4} + \frac{\psi_N}{\tau_5} + \frac{1 - \psi_N - \psi_C}{\tau_6} \right\} X_C$$

$$+ \frac{\psi_N}{\tau_7} \frac{\exp(\theta_C)}{\exp(\theta_N)} \left\{ \frac{X_C(1 - X_N)}{1 - \exp(-\theta_N)} - \frac{X_N(1 - X_C)}{1 - \exp(-\theta_C)} \right\} (1 - \exp(-\theta_C)) \quad (9)$$

where

$$X = (\bar{E} - E)/\bar{E}.$$

In the above equations the subscripts N and C refer to nitrogen and carbon monoxide respectively, ψ denotes the component mole fraction. E is the energy contained within the vibrational mode per mole of component, $\bar{E}$ is the equilibrium value at the bulk gas temperature T, and $\theta = \theta_v/T$. where θ_v is the characteristic vibrational temperature of the molecular component ($\theta_{v,N} = 3350°K$ and $\theta_{v,C} = 3090°K$). The times τ_1, ..., τ_7, are the characteristic vibrational relaxation times for the forward going directions of reactions (1)-(7). The characteristic time τ_7, may be expressed in terms of a probability as

$$\tau_7 = \{P(N_2^{10}, CO_{01})Z_{NC}\}^{-1} \quad (10)$$

where $P(N_2^{10}, CO_{01})$ is the probability that during a collision an N_2 molecule undergoes the vibrational transition from level $v = 1$ to $v = 0$, whereas the CO molecule undergoes the transition from $v = 0$ to $v = 1$. Z_{NC} is the collision frequency of the N_2 with the CO molecules.

Since the energy discrepancy between the vibrational level spacings of CO and N_2 is only 187 cm^{-1}, Eqs. (8) and (9) may be simplified by assuming $\theta_N \simeq \theta_C$. Thus, we obtain

$$- dX_N/dt = aX_N - b(X_C - X_N) \tag{11}$$

and

$$- dX_C/dt = cX_C + d(X_C - X_N) \tag{12}$$

where,

$$a = \left(\frac{\psi_N}{\tau_1} + \frac{\psi_C}{\tau_2} + \frac{1 - \psi_N - \psi_C}{\tau_3} \right), \qquad b = \psi_C/\tau_7$$

and

$$c = \left(\frac{\psi_C}{\tau_4} + \frac{\psi_N}{\tau_5} + \frac{1 - \psi_N - \psi_C}{\tau_6} \right), \qquad d = \psi_N/\tau_7$$

By assuming that the bulk gas temperature T remains constant during the relaxation process, we obtain

$$X_C = A \exp(- rt) + B \exp(- qt) \tag{13}$$

as the general solution to Eqs. (11) and (12). The parameters r and q are simple algebraic functions of a, b, c, and d, and the constants A and B are determined by satisfying the boundary conditions: $X_C = 1$, and $dX_C/dt = - c$, at zero time.

Since the experimental measurement of the infrared emission profiles provides a measure of X_C as a function of time,[9] i.e.,

$$X_C(t) \simeq (I_o - I(t))/I_o, \tag{14}$$

where I_o is the equilibrium emission intensity corresponding to $E = \bar{E}(T)$, a semi-logarithmic plot of X_C versus time yielded the values of A, B, r, and q. The composite values of the characteristic relaxation times, a^{-1}, b^{-1}, c^{-1}, and d^{-1}, could then be calculated.

4. EXPERIMENTAL RESULTS

Initially, a series of experiments were carried out using a test gas mixture containing 2.5 mole per cent of CO in argon in order to establish that the characteristic vibrational relaxation times, τ_6, measured using our system were in agreement with previous experimental results. The measurements of τ_6, which were obtained from the slope of semi-logarithmic plots of $(I_o - I(t))/I_o$ versus time, were found to be in excellent agreement with the previous results of Millikan and White, [10] as will be shown below.

Figure 1a shows an oscilloscope record of the infrared emission signal obtained using a test gas mixture containing 2.5 mole per cent CO and 10 mole per cent N_2 in argon. The oscilloscope record in Figure 1b was recorded using a slower time base. It shows the same infrared emission signal together with the signal output derived from the end wall pressure transducer. It can be seen that the disturbance caused by bifurcation of the reflected shock wave reaches the end wall about 260 μ sec from the instant of shock reflection. However, it is also apparent that the vibrational relaxation process is essentially complete before the bifurcation disturbance reaches the end wall, as witnessed by the small plateau in the infrared emission signal between about 220 and 260 μ sec after shock reflection. Thus, it is possible to determine I_o from the trace shown in Fig. 1b with good accuracy.

Figure 2 shows the semi-logarithmic plot of $(I_o - I(t))/I_o$ versus

time obtained from Figs. 1a and 1b. The effect of the added nitrogen in
the test gas is clearly seen, i.e., two distinct relaxation times can be
identified in accordance with the two exponential terms contained in
Eq. 13. From such results as those shown in Figs. 1 and 2, it was a
simple matter to determine A, B, r, and q, and thus to calculate the
values of the characteristic times, a^{-1}, b^{-1}, etc. The bulk gas tempe-
rature for the assumed isothermal relaxation process was calculated as
the average of the two reflected shock temperatures corresponding to
vibrationally unexcited molecules and vibrational equilibrium. The
temperature uncertainty which this assumption introduced was found to
be less than the experimental scatter of the relaxation measurements.

Figure 3 illustrates the experimentally measured values of pc^{-1}
(solid points) and our measurements of $p\tau_6$ (open circles) plotted in
the usual Landau-Teller form. The open circles are seen to agree very
closely with the previous measurements of $p\tau_6$ by Millikan and White[10]
which are represented by the full line. Although our measurements of pc^{-1}
appear to depart slightly from the measurements of $p\tau_6$ at the lowest
temperatures, we do not believe that the results as a whole confirm this
trend unambiguously, and therefore, conclude that over the temperature
range 2000°-4000°K, argon and nitrogen are about equally efficie t as
T-V collision partners in relaxing CO.

Figure 4 shows a Landau-Teller plot of our measurements of pa^{-1}.
The upper full line represents measurements of $p\tau_1$, again from Millikan
and White,[10] which had previously been found to correlate with the

higher temperature measurements of $p\tau_1$ by Appleton.[11] The lower full line represents measurements of $p\tau_1$ obtained by Tsuchiya,[12] and the lower dashed line represents his measurements of $p\tau_3$. It is clear that our measurements of pa^{-1} show argon to be a less efficient T-V collision partner than nitrogen in relaxing nitrogen molecules. From a statistical evaluation of these measurements in which account is taken of the different gas compositions, and by assuming that $\log_{10}(p\tau_3)$ varies linearly with $T^{-1/3}$ such that it passes through the point of "common origin" determined by Millikan and White (see Fig. 1, Ref. 10), the following emirical correlation formula was obtained:

$$\log_{10}(p\tau_3) = 109 \ T^{-1/3} - 11.3 \tag{15}$$

which is shown by the upper dashed line in Fig. 4. This rather arbitrary method of correlating the data was used simply because the scatter of our measurements did not allow an unambiguous determination of the temperature dependance of $p\tau_3$ to be made for the limited temperature range of the experimental results.

Figure 5 illustrates our experimental determinations of the V-V energy exchange probability, $P(N_2, {}^{10}_{01} CO)$, as a function of temperature. The open circles correspond to the results given by Sato, Tsuchiya, and Kuratani.[4] The crosses represent the experimental measurements by von Rosenberg, Bray, and Pratt,[6] and the full line shows the variation of the probability calculated using method A of the SSH theory[5] for which values of the molecular parameters were taken from those listed by Taylor, Camac, and Feinberg.[1] The dashed line is simply a least squares fit to the experimental measurements.

5. DISCUSSION OF RESULTS

It is apparent from the results shown in Fig. 4 that our estimate
of $p\tau_3$ is between a factor of 1 and 2 greater than that given by Tsuchiya.[12]
However, because Tsuchiya measured lower values for $p\tau_1$ than we assumed
in our data analysis (compare full lines in Fig. 4), the ratio of the
characteristic times, τ_3/τ_1, obtained from the separate results of each
investigation is about the same; i.e., over the temperature range 2000°-
$4000^{\circ}K$, argon is between a factor of 2 and 3 less efficient than nitrogen
for the T-V relaxation of nitrogen. The reason for the differences between
the measurements of $p\tau_1$ reported by Tsuchiya and the measurements of other
investigators[10,11] is not clear. We can only suggest that this discre-
pancy results from the different measuring techniques used and therefore
may reflect the combined uncertainty of the measurements.

It can be seen from Fig. 5 that the three sets of experimental shock-
tube data for $P({}^{10}_{01}N_2, CO)$ show a consistent trend and, within the mutual
experimental scatter, are in quite good agreement with one another. Although
our measurements and the SSH theory prediction appear to agree at the highest
temperatures, it is apparent that the theory overestimates the probability
by about a factor of ten at $2000^{\circ}K$. This observed departure of the meas-
urements from theory is similar to that reported by Taylor, Camac, and
Feinberg[1] and by Taylor and Bitterman[13] who measured the V-V energy
exchange probability between N_2 and the ν_3 mode (assymmetric stretch) of
CO_2. These investigators also found V-V energy exchange probabilities which
were significantly lower than the corresponding SSH theory predictions over
the approximate temperature range 1300°-$2500^{\circ}K$. The most logical explanation
for the discrepancy between theory and experiment appears to be that the

theory assumes the close encounter collisions which are responsible

for energy transfer to be too impulsive; i.e., the repulsive part of

the Lennard-Jones potential which was used to calculate the probabili-

ties[5] is too steep.

Below about $1000^{\circ}K$, Taylor and Bitterman[13] and Rosser, Wood,

and Gerry,[14] who used a laser-excited vibrational fluorescense

technique, observed that the probability $P(CO_2(\nu_3)^{10}_{01}, N_2)$ increased with

decreasing temperature. This behaviour appears to be fully explained

by the recent theory of Sharma and Brau[15] which assumes that the energy

transfer is accomplished via the long-range quadrupole-dipole forces

between N_2 and CO_2. The experimental minimum in $P(CO_2(\nu_3)^{10}_{01}, N_2)$ is thus

observed[13] at about $1300^{\circ}K$ where the contributions to the probability

from the long-range and short-range interactions are comparable. Unfortu-

nately, insufficient data are available for the $CO-N_2$ system to show

whether a minimum value of $P(N_2^{10}_{01}, CO)$ is attained. As can be seen in

Fig. 5, the room temperature data[16-18] gives little help in resolving

this matter due to the large discrepancies between the individual meas-

urements.

6. CONCLUSIONS

On the basis of this investigation where vibrational relaxation rates were measured in mixtures of CO, N_2, and Ar over the approximate temperature range 2000°-4000°K, the following conclusions may be drawn:

(i) argon and nitrogen are about equally efficient as T-V collision partners for vibrational relaxation of carbon monoxide,

(ii) argon is between a factor of 2 and 3 times less efficient than nitrogen as a T-V collision partner for the vibrational relaxation of nitrogen molecules, and

(iii) although the measured V-V energy exchange probability, $P(N_2, CO)_{01}^{10}$, agrees fairly well with the SSH theory prediction at 4000°K, the measured probability is about a factor of 10 times smaller than the theoretical prediction at 2000°K.

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FIGURE CAPTIONS

Figure 1a Infrared emission record. Test gas: 2.5 mole per cent CO,
10.0 mole per cent N_2, 87.5 mole per cent Ar. Primary shock
Mach number M_s = 3.54, initial pressure p_1 = 45 torr.
Reflected shock temperature T_5 = 2670°K, reflected shock
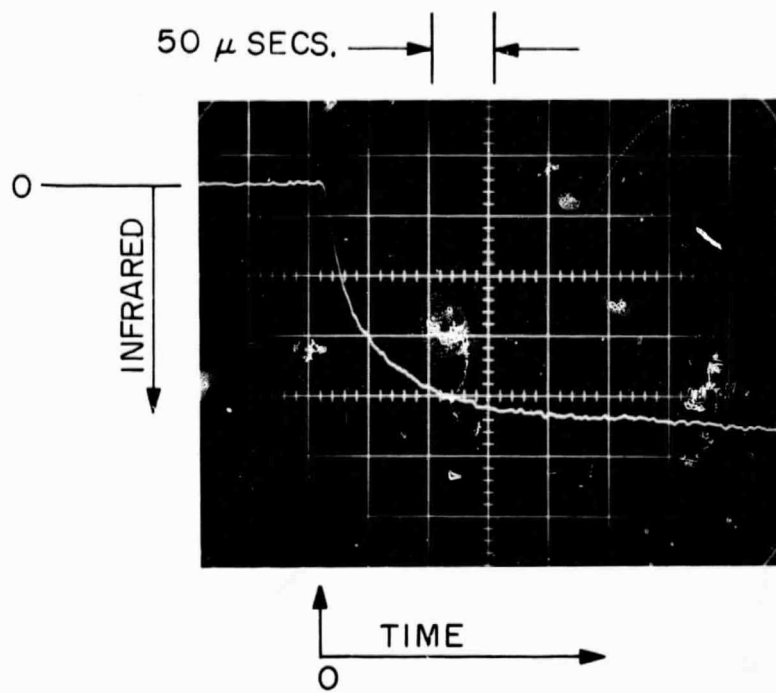pressure p_5 = 4.38 atm.

Figure 1b Infrared emission and pressure transducer signals recorded
using extended time base. Same experiment as for Fig. 1a.

Figure 2 Data plot of $(I_o - I(t))/I_o$ versus time taken from Fig. 1.
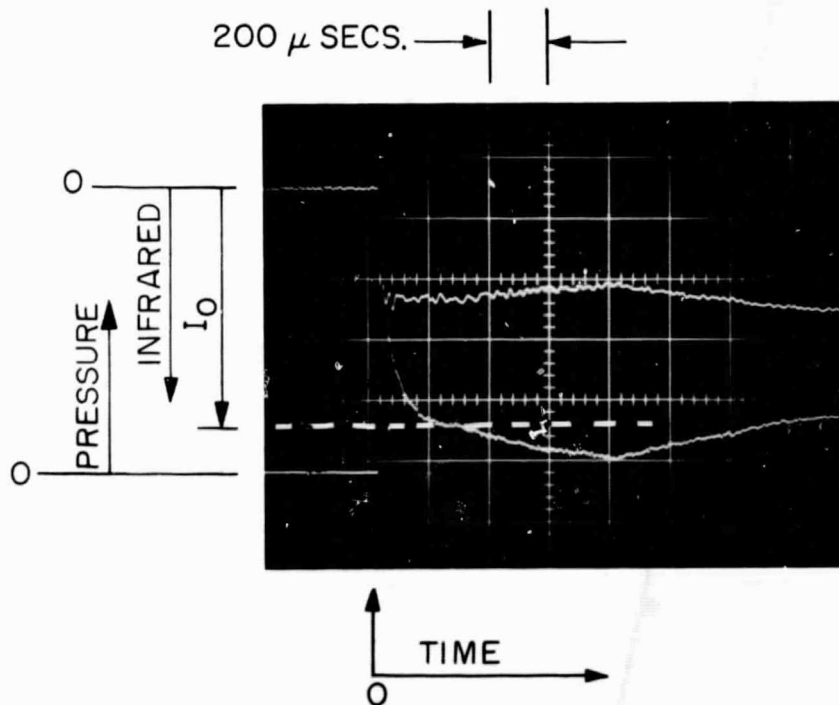
Figure 3 Landau-Teller plot of characteristic vibrational relaxation
times τ_6 and $c^{-1} = \{\psi_C/\tau_4 + \psi_N/\tau_5 + (1 - \psi_N - \psi_C)/\tau_6\}^{-1}$.

Figure 4 Landau-Teller plot of characteristic vibrational relaxation
times τ_1, τ_3, and $a^{-1} = \{\psi_N/\tau_1 + \psi_C/\tau_2 + (1 - \psi_N - \psi_C)/\tau_3\}^{-1}$.
The point symbols have the same meaning as in Fig. 3.

Figure 5 Plot of the V-V energy exchange probability $P(N_2, CO)_{01}^{10}$ as a
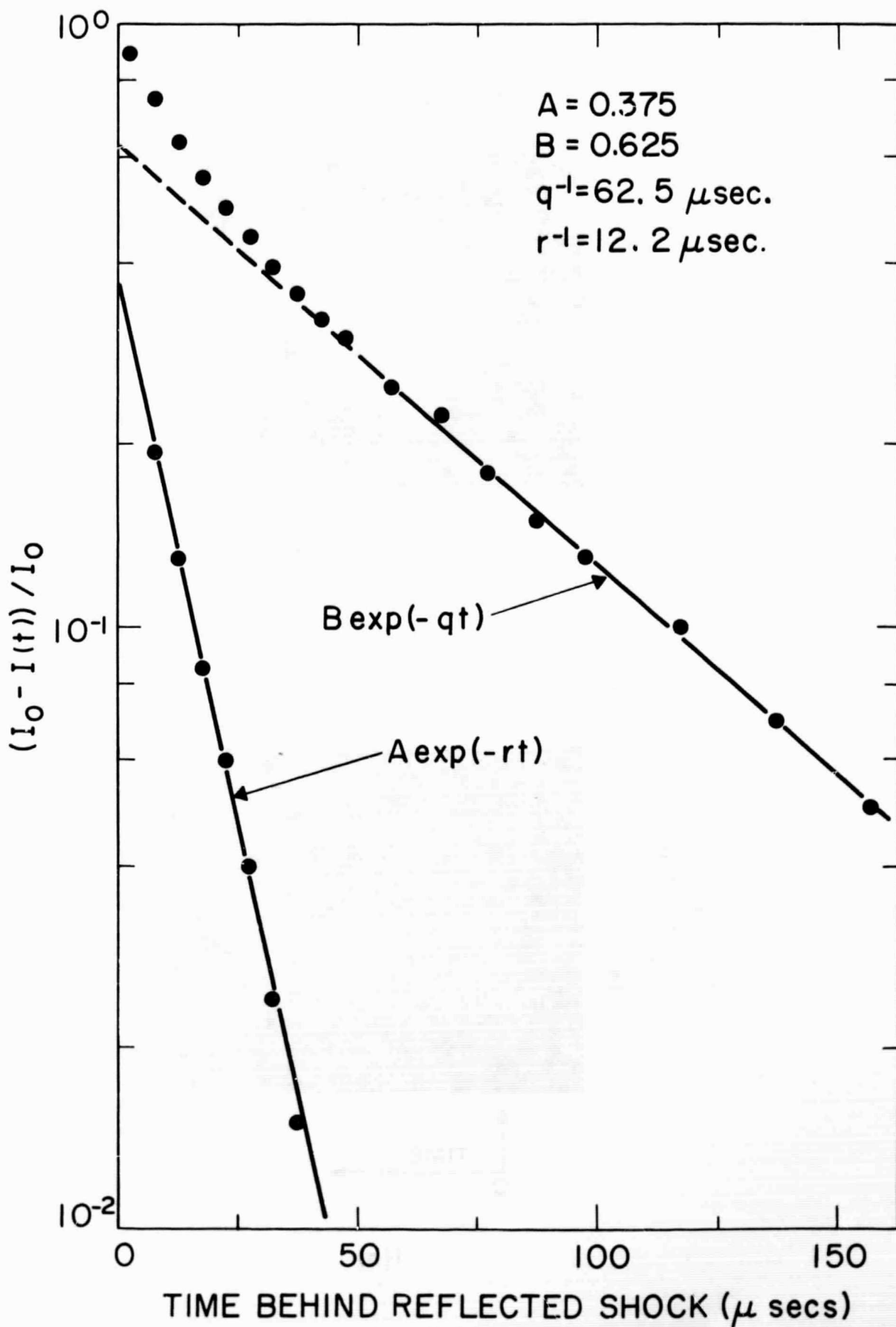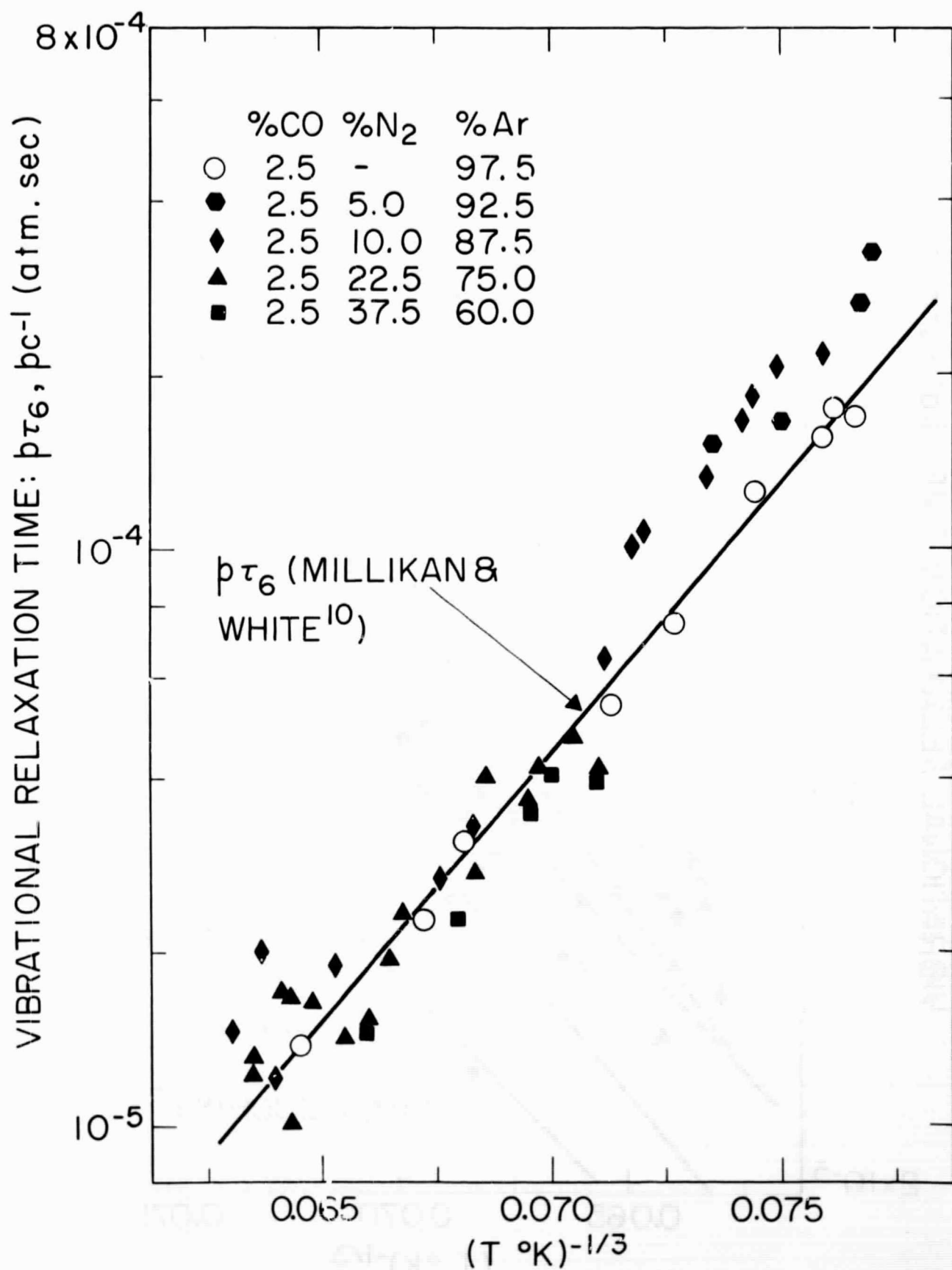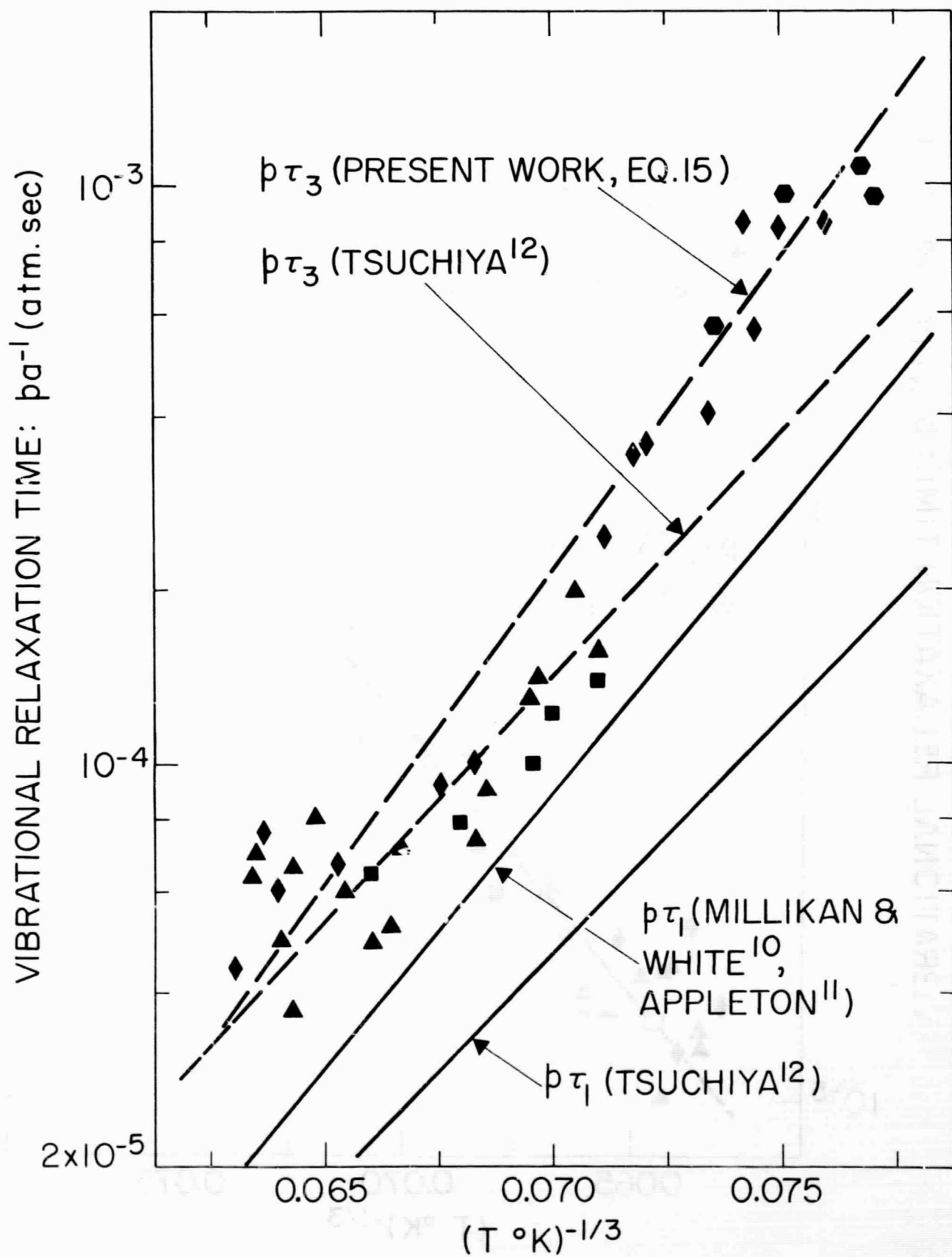function of temperature. The solid symbols have the same
meaning as in Fig. 3.

50 μ SECS.

O

INFRARED

TIME

O

1(a)

200 μ SECS.

O

PRESSURE

INFRARED

I_0

O

TIME

O

1(b)

FIGURE 2

FIGURE 3
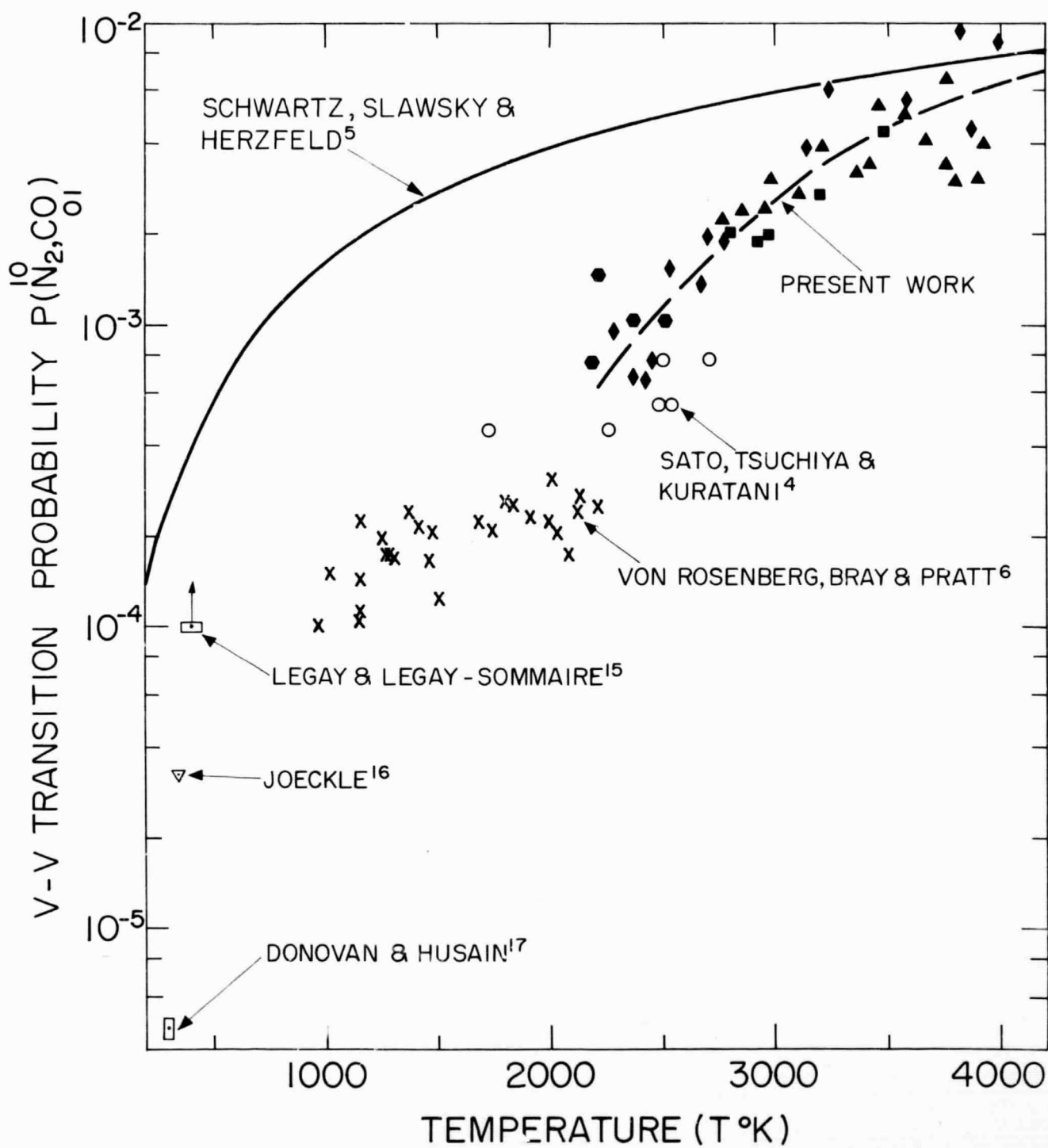
FIGURE 4

FIGURE 5

DOCUMENT CONTROL DATA - R&D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

1. ORIGINATING ACTIVITY (Corporate author)	2a. REPORT SECURITY CLASSIFICATION
Massachusetts Institute of Technology Cambridge, Massachusetts	Unclassified
	2b. GROUP

3. REPORT TITLE

Shock-Tube Measurements of the Vibration-Vibration Energy Exchange Probability for the CO-N$_2$ System

4. DESCRIPTIVE NOTES (Type of report and inclusive dates)

5. AUTHOR(S) (Last name, first name, initial)

McLaren, Thomas I. and Appleton, John P.

6. REPORT DATE	7a. TOTAL NO. OF PAGES	7b. NO. OF REFS
November 1970	17	18

8a. CONTRACT OR GRANT NO. NASA NAS2-4919	9a. ORIGINATOR'S REPORT NUMBER(S)
b. PROJECT NO.	Fluid Mechanics Laboratory Publication No. 70-10
c. ONR N0014-67-A-0204-0040	9b. OTHER REPORT NO(S) (Any other numbers that may be assigned this report)
d. ARPA Order No. 322	

10. AVAILABILITY/LIMITATION NOTICES

Distribution Unlimited

11. SUPPLEMENTARY NOTES	12. SPONSORING MILITARY ACTIVITY
	Advanced Research Projects Agency of the Dept. of Defense. Office of Naval Research Washington, D. C.

13. ABSTRACT

A shock-tube study was carried out to measure the vibration-vibration energy exchange probability, $P_{01}^{10}(N_2, CO)$, in N$_2$/CO/Ar mixtures. It was determined that at a temperature of about 4000°K, the measured probability, $P_{01}^{10}(N_2, CO) \simeq 8 \times 10^{-3}$, agrees fairly well with the theoretical prediction of Schwartz, Slawsky, and Herzfeld (SSH), but that with decreasing temperature the measured probability falls considerably below the SSH theory prediction; i.e., $P_{01}^{10}(N_2, CO) \simeq 4 \times 10^{-4}$ (measured) and $P_{01}^{10}(N_2, CO) \simeq 4 \times 10^{-3}$ (SSH), at 2000°K. The experimental results also demonstrate that over the temperature range 2000°-4000°K, argon and nitrogen are about equally efficient as translation-vibration collision partners for vibrational relaxation of CO, whereas, argon is between 2 and 3 times less efficient than N$_2$ for vibrational relaxation of N$_2$ molecules.

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14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Shock–Tube						
Carbon Monoxide						
Nitrogen						
Infrared Emission						
Vibrational Relaxation						
Vibration-Vibration Energy Exchange Probability						

INSTRUCTIONS

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